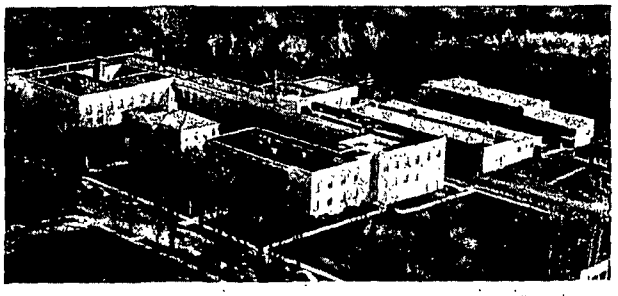

THE INSTITUTE OF PAPER CHEMISTRY, APPLETON, WISCONSIN

NU NUMBER OF PULP

Project 2634 - Report

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THE INSTITUTE OF PAPER CHEMISTRY
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NU NUMBER OF PULP

INTRODUCTION

The following is the first attempt to "standardize" the procedure for the Nu Number test for routine manual use in a pulp mill. The Nu Number is, of course, a direct function of the lignin content of most pulps up to about 70% yield. Above about 70% yield, the Nu Number is not usually a good test for the lignin content of most pulps, but may be a direct function of yield in this range, based on limited laboratory examination of hardwood NSSC (Na-base) pulps.

When applying the following procedure to pulp above about 60% yield, the sample size specified (0.250 g.) may not be suitable because the relatively high lignin content will result in a rather high light absorbance value for the HNO_3 extract. Therefore, for pulps above 60% yield, use a sample of 0.175 gram and change the factor of 250 in the numerator of the equation in the "Calculation" section to 175.

Additional minor modifications in the procedure may be required if a dual-beam spectrophotometer is not available. Any color-measuring device may be used that will yield reliable results. Single-beam colorimeters that use test tubes as cuvettes are suitable too; but if 15-mm. diameter test tubes are used, the absorbance values may be too high for accurate measurement. In this case, use a smaller pulp sample, as outlined in the preceding paragraph. When using single-beam instruments, the "blank" will, of course, be 14% HNO_3.

Perhaps the most important step in the whole procedure is that of moisture determination of the pad of pulp to be used as the sample. If this is not accurate, the Nu Number determination will be proportionately erroneous.

As experience with this procedure accumulates, a modified procedure may be issued in the future.

EQUIPMENT

1. Constant-temperature water bath, 85 ± 1°C.
2. Spectrophotometer or colorimeter, preferably a dual-beam instrument such as the Beckman DB, with matched 10-mm. pyrex cells.
3. Beakers, tall form, 300-ml. capacity (Corning no. 1060) with watch-glass covers.
4. Test tubes, low actinic, 18 x 150 mm., Corning no. 59800.
5. Funnels with about 1/2-in. stems, 55-mm. rim diameter.
6. Test tube rack.
7. Two hundred fifty-ml. graduated cylinder.
8. Glass stirring rod, about 6 in. long.
9. Buchner funnel, about 125 mm. i.d.
10. Filter flask, 2 liter.
11. Filter paper, Whatman no. 40 or equivalent, 9-cm. and 11-cm. diameter.
12. Noble & Wood hot-plate-type drier, or equivalent.
13. "Hot balance," analytical type, for weighing moisture pad.
14. Analytical balance.
15. Stopwatch.
16. Two pyrex weighing bottles with ground-glass caps, approx. 25-mm. dia. x 40 mm. high.
17. Pyrex weighing bottle with ground-glass cap, approx. 40-mm. dia. x 100 mm. high.

REAGENTS

1. Fourteen percent nitric acid. Dilute 200 ml. of concd. HNO_3 (usually 69-71% by wt. HNO_3) to 1 liter with distilled water.

Since the concentration of the concd. HNO_3 will vary somewhat from jug to jug, it may be best to make up a large supply (10-20 liters of 14% HNO_3 at a time.

2. Potassium dichromate ($K_2Cr_2O_7$) standard. Weigh exactly 100 milligrams of dry primary standard-grade $K_2Cr_2O_7$ on an analytical balance, dissolve it in distilled water and dilute it to exactly 1 liter in a volumetric flask. The pH should be 4.8-5.1.

REACTION RATE CURVE

Before routinely making Nu Number tests, it is essential to determine the optimum reaction time of the pulp with nitric acid. Most softwood kraft pulp will have the same optimum reaction time, regardless of the mixture of ordinary softwoods used. Hardwoods will not, however, have the same reaction time as softwoods, even though cooked by the same process. A given species of softwood cooked by two different processes (kraft vs. sulfite) will then usually exhibit different optimum reaction times also.

Using the exact procedures described in the succeeding sections, weigh out five pulp samples and leave them in the water bath for 3, 6, 9, 12, and 15 minutes, respectively. Calculate the Nu number of each and plot the Nu number against reaction time. The data points will form a curve that goes through a maximum Nu number. The reaction time at which this maximum occurs is the optimum reaction time and should be used in all subsequent Nu Number tests on this pulp.

Serious variation in wood mixture being cooked (particularly a rise or fall in hardwood content), cooking conditions, or chemicals variations should be considered cause for again determining the optimum reaction time.

SAMPLE PREPARATION

The pulp must be well washed and screened since the presence of black liquor solids will cause turbidity in the nitric acid solution placed in the colorimetric cuvettes, leading to high results. Dissolved lignin in black liquor will also react with nitric acid, again leading to high results.

Place a disk of filter paper (11-cm. dia.) in the Buchner funnel and make a thin pad of pulp not more than 1/32 in. thick by vacuum filtration. After the water has all drained through the pad, leave the vacuum on for a minute or two to remove additional moisture by drawing air through the pad. Remove the pad, peel off the filter paper and discard it, cut the pulp pad in half, immediately place one half in a small plastic bag, press the air from the bag, and fold the end closed. Use the other half for moisture determination by placing it in the large weighing bottle (tared) and obtaining its wet weight; then place it between two pieces of blotter stock, dry the "sandwich" on the hot-plate-type drier with frequent turning until steam nearly ceases to be given off. At this point, remove the pulp pad from between the blotters and finish drying it directly on the drier. Obtain its dry weight on the "hot balance."

Use portions of the remaining half of the pulp pad (in the plastic bag) for the Nu Number test. Based on the moisture content, weigh out in the smaller weighing bottles duplicate samples equivalent to 0.250 gram o.d. pulp. The exact weight must be known to the nearest 0.001 gram, but the amount may vary by ±0.005 g. o.d. Place each sample in a 300-ml. tall-form beaker and add exactly 200 ml. of 14% nitric acid. Place the beakers in the water bath, start the stopwatch, and stir the mixture for about 2 minutes with a glass rod to disperse the pulp and to help bring the liquid up to temperature more quickly. Cover the beakers with a watch glass, and stir for about 10 seconds at 2-minute intervals until the end of

the reaction period. The beakers should be immersed in the constant-temperature bath so that the liquid level in the beaker is at least 1/2 inch below the bath water surface.

At the end of the reaction period, remove the beakers from the bath and immediately filter about 25 ml. into low-actinic test tubes, using the 55-mm. rim diameter funnels and the 9-cm. filter paper, with the funnel resting directly in the test tube. When the test tube is full, cool it by holding it in a stream of tap water for about 1 minute. This should cool it to below 30°C.

COLOR MEASUREMENT

Assuming that a dual-beam spectrophotometer is used for color measurements, set the monochromator for 425 nm. Adjust the instrument for zero transmittance with an opaque block in the sample compartment and nothing, not even the empty cuvette, in the reference compartment. The 100% transmittance adjustment is made with both cells filled with 14% HNO_3. Leaving the reference cell filled with 14% HNO_3, rinse the sample cell twice with the cooled filtrate in the test tube, and finally fill it, insert it in the sample compartment, and measure the light absorbance.

Immediately after completion of a series of absorbance measurements of cooled filtrates from the pulp-HNO_3 reaction, rinse the sample cuvette several times with distilled water, then once with the $K_2Cr_2O_7$ standard, and measure the absorbance of the standard, still leaving the reference cell filled with 14% HNO_3. This value should be between 0.160 and 0.165 at 23°C. and pH 4.8-5.1, and should vary little from day to day. Variations outside these limits indicates either a need for a fresh standard or that something is not quite right with the spectrophotometer (dirty cuvette, etc.).

CALCULATION

Let: $\underline{A}_s$ = absorbance of filtered HNO_3-pulp mixture,

$\underline{A}_{std.}$ = absorbance of $K_2Cr_2O_7$ standard, and

$\underline{W}_s$ = milligrams o.d. pulp sample.

Then,

$$Nu = \frac{100 \times A_s \times 250}{A_{std.} \times W_s} .$$

The variation in Nu number between duplicate samples should not exceed ± 2% of the mean value of the two. The mean value of the duplicates should be taken as the Nu number of the pulp.

ILLUSTRATION

Figure 1 illustrates the general relationship between Kappa number and Nu number obtained by this procedure. The pulps used in establishing the regression line are from seven different pulp mills from widely scattered geographical locations in the United States. Some were produced in Kamyr digesters and some in batch digesters, and they represent six different wood species. The relative deviation ($\underline{S}_{rel.}$) should be smaller for a given individual pulp mill.

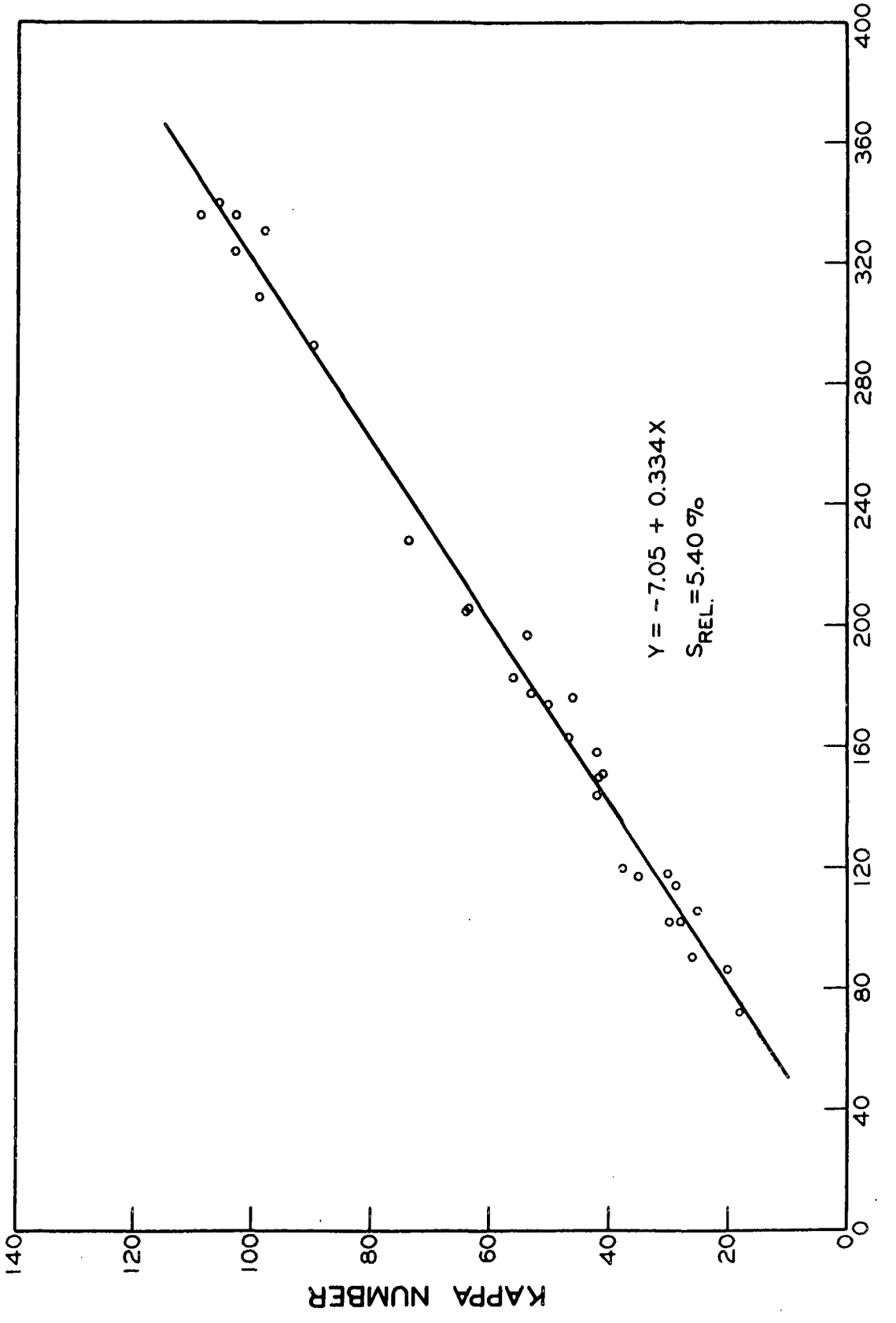

Figure 1. Relationship Between Kappa Number and Nu Number for Unbleached Softwood Kraft Pulp